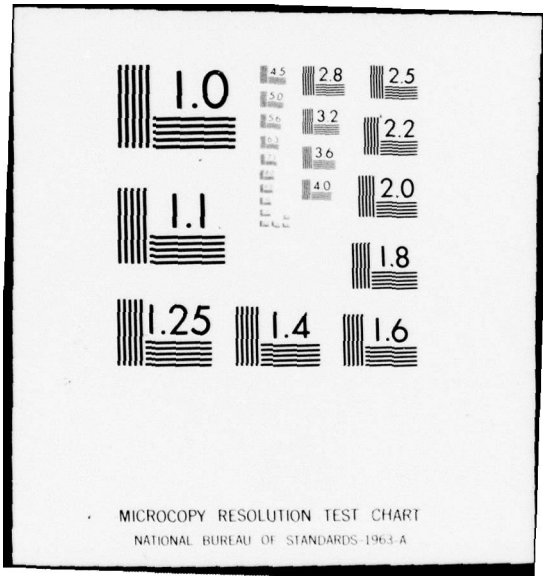
AD-A039 702 BOSTON UNIV MASS DEPT OF CHEMISTRY F/G 7/4
PHOTON ENERGY STORAGE IN ORGANIC MATERIALS: THE CASE OF LINKED --ETC(U)
MAR 77 G JONES, W R BERGMARK, T E REINHARDT N00014-76-C-0442
UNCLASSIFIED NL

1 OF 1
AD A039 702

END

DATE
FILMED
6-77


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0442

Project No. NR 051-574

TECHNICAL REPORT NO. 6

PHOTON ENERGY STORAGE IN ORGANIC MATERIALS: THE CASE OF LINKED ANTHRACENES

by

G. Jones, II, W.R. Bergmark, and T.E. Reinhardt

Prepared for Publication
in
Solar Energy

Department of Chemistry
Boston University
Boston, Massachusetts 02215

March 15, 1977

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Technical Report No. 6, 1 Nov 75 - 31 Dec 76,	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle): Photon Energy Storage in Organic Materials: The Case of Linked Anthracenes,	5. TYPE OF REPORT & PERIOD COVERED: Technical, 11/1/75 - 12/31/76
	6. PERFORMING ORG. REPORT NUMBER: 15
7. AUTHOR(s): G. Jones, II, W.R. Bergmark, and T.E. Reinhardt	8. CONTRACT OR GRANT NUMBER(s): N00014-76-C-0442
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, Boston University, Boston, Massachusetts 02215	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: NR 051-574/9-26-75 (472)
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, 800 North Quincy Street, Arlington, Virginia 22217, DODAAD Code N00014	12. REPORT DATE: March 15, 1977
	13. NUMBER OF PAGES: 26
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): (10) Guilford Jones, II, William R. Bergmark, Thomas E. Reinhardt	15. SECURITY CLASS. (of this report): unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited.

(11) 15 Mar 77

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

(12) 30p.

18. SUPPLEMENTARY NOTES

Prepared for publication in Solar Energy

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Photochemical conversion of solar energy, anthracene photodimerization, chemical storage of solar energy, valence photoisomerizations, energy storing reactions, cyclic photochemistry, photocalorimetry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Criteria for the photochemical storage of solar energy as latent heat are outlined. Energy-storing valence isomerizations which may be driven by irradiation and which may be reversed by heating with or without a catalyst are described. Data for photoisomerizations which utilize 300-500 nm radiation with storage capacities of 50-250 cal/g and with storage efficiencies of 5-10% are summarized. New data concerning linked anthracenes which photoisomerize with Φ = 0.2-0.4 are provided. A photocalorimeter for the measurement of storage enthalpies is described. New systems for the practical conversion of solar energy are suggested.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-014-6601

401003

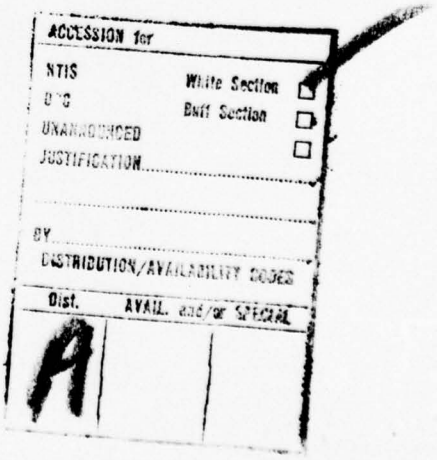
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

PHOTON ENERGY STORAGE IN ORGANIC MATERIALS: THE CASE OF LINKED ANTHRACENES[1]

Guilford Jones, II,[2a] William R. Bergmark,[2b] and Thomas E. Reinhardt[2a]

Departments of Chemistry, Boston University, Boston, MA 02215

and Ithaca College, Ithaca, NY 14850



ABSTRACT

Criteria for the photochemical conversion of solar energy are reviewed in terms of utilization of photoactive organic materials. Endoergic valence isomerizations which may be driven by visible light are proposed for study. These isomerizations store electronic excitation energy as chemical potential energy. Products of the proposed photoreactions are kinetically stable for energy storage over controllable periods. Stored energy is retrieved by thermal or catalytic recycling to the original photoactive substance. Such organic materials are potentially useful as additives to working fluids of conventional solar-thermal conversion units. Photon energy storage is illustrated in several examples which utilize 300 - 500 nm radiation for isomerizations with storage capacities of about 100 cal/g. New data including quantum efficiencies, storage capacities, and conditions for recycling are presented for a series of linked anthracenes. A photocalorimeter capable of direct measurement of storage enthalpies is described. The economic and physical requirements of a photochemical storage material are outlined, and several systems for the conversion of solar energy on an appropriate scale are suggested.

INTRODUCTION

Several excellent reviews[3] have outlined advantages and criteria for successful photochemical conversion of solar energy. Chief among the benefits in storage of light energy as chemical potential energy in relatively stable molecules, ions, etc., is the potential solution in certain contexts to the vexing problem of solar power intermittency. Photoformation of a chemical 'fuel' could provide a source of energy during periods of low or negligible solar intensity. Although organic dye - metal redox systems which produce photogalvanic effects are well known,[4] systems which are strictly organic chemical in nature have not been thoroughly considered in terms of photochemical storage solar energy. We wish to outline strategies for selection of organic materials for potential use in solar-thermal energy conversion units and to describe several systems which store modest amounts of solar energy and which illustrate the principles.

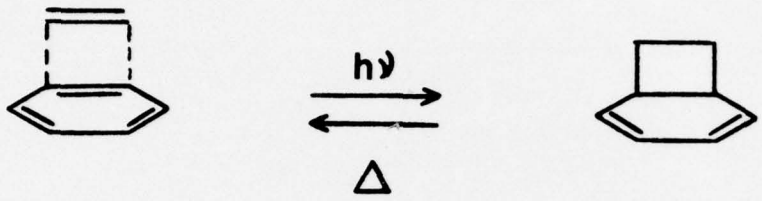
A practical photochemical energy conversion system is described in Table I in terms of criteria[3,5] for efficient use of a closed cycle of reactants and observations[6] appropriate for use of organic materials and products. The simplest plan requires a reaction, A ⟶ B, which can be driven in one direction photochemically and thermally in the reverse. The amount of energy given off in the reaction B ⟶ A represents the energy stored in the photochemical step. This "in situ" energy conversion requires no separation of materials A and B (e.g., the separation of a gas as by-product from the mixture as in thermal storage cycles[7]) nor the introduction of a new chemical (other than perhaps a catalyst, vide infra) in order to complete the cycle.

Table I. Requirements for the Organic Photochemical Conversion of Solar Energy

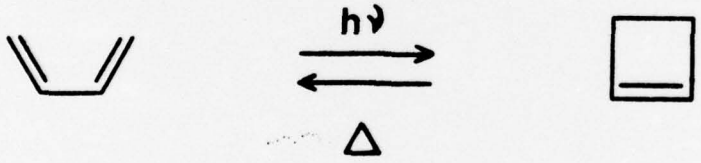
IMPERATIVE	OBSERVATION
$A \xrightarrow{h\nu} B$ $B \longrightarrow A + \text{heat}$	
1. Reactant A must absorb or be sensitized to ultraviolet and visible light.	Monophotonic photochemistry at > 700 nm is quite unlikely; useful range = 300 - 700 nm (40 - 90 kcal/Einstein), ~50% of total solar energy.
2. Photoproduct B must not competitively absorb (or quench sensitizer).	Reaction A → B should be photochromic (decrease in the degree or continuity of unsaturation in A).
3. The quantum yield for reaction A → B must be near unity.	Intramolecular reactions should be favored over intermolecular ones; luminescence should not be competitive.
4. Reaction A → B must have a large positive ground state enthalpy.	Selected valence photoisomerizations with ΔH = 10 - 30 kcal/mol are known; reactions should be selected in which small rings are generated and/or aromaticity disrupted.
5. Photoproduct B must be (kinetically) stable.	Orbital topology restrictions for selected isomerizations inhibit B → A; reversions at 50 - 100° will be useful.
6. A chemical control external to the cycle A ⇄ B may be used to initiate B → A.	Metal or acid catalysts may be suitable.
7. Reactant A (B) must be inexpensive.	Availability on an industrial scale eventually required. Cost should be < $1.00/lb (vide infra).
8. Materials must not be dangerous or difficult to handle.	Chemicals which are toxic or which require unusual atmospheres or pressures should be avoided.

The most promising candidates for interconversions of the type $A \rightleftarrows B$ are isomerizations of organic molecules, many of which may be cleanly driven photochemically and/or thermally. A blend of factors enables organic materials to store electronic excitation energy efficiently and permanently. Properly selected organic isomerization systems have significant storage enthalpies because large destabilizing bond angle strain energies[8] may be gained or stabilizing resonance energies[9] may be lost during photoisomerization. In addition, orbital topology or symmetry constraints[10] enable energy rich photoproducts to withstand a substantial thermodynamic driving force for back reaction by erecting kinetic barriers to reversion. Ideally these barriers can be circumvented when desirable through catalysis. Although no organic photochemical (latent heat) storage system which makes efficient use of solar energy is yet known, a number of prototypes have been examined, and some feasibility for the cyclic scheme is suggested.

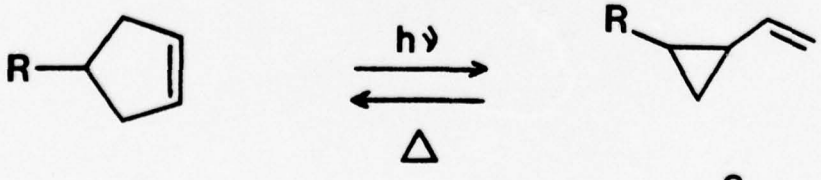
Classes of energy storing photoreactions are shown below. They include the cycloaddition of aromatic and ethylenic pi components ($\underset{\sim}{1} \rightarrow \underset{\sim}{2}$) the "electrocyclic" or ring-chain isomerization of a butadiene moiety ($\underset{\sim}{3} \rightarrow \underset{\sim}{4}$), and the "sigmatropic" contraction of a cyclic compound ($\underset{\sim}{5} \rightarrow \underset{\sim}{6}$). Storage enthalpies ($-\Delta H$, back reaction) for these photoisomerizations of 20, 10 and 20 kcal/mol may be estimated by consideration[9] of bond and resonance energies and ring strain. Examples of all three reaction classes are known[11] and in most cases energy-rich photoproducts are <u>kinetically</u> stable at ambient temperatures.



1 2



3 4

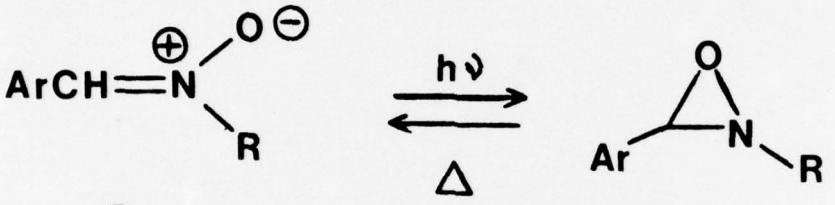


5 6

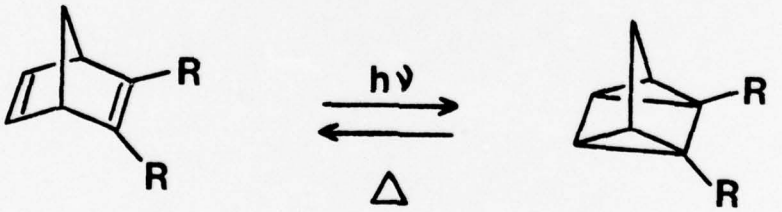
PHOTOCHEMICAL STORAGE PROTOTYPES

The only photochemical system which has been thoroughly studied in terms of storage of solar energy ostensibly as latent heat (with which organic systems might be compared) is the equilibrium, $NOCl \rightleftharpoons NO + 1/2\ Cl_2$. The data, which have been reviewed by Marcus and Wohlers[12] indicate a reasonable storage capability. Nitrosyl chloride is highly colored, photochemically active over much of the visible range with good solution quantum yield (ϕ = 0.7 - 1.1) for decomposition and a photoreaction enthalpy of 4.9 kcal/mol. Along with the relatively low enthalpy however, the back reaction is problematic since the colorless nitric oxide and (molecular) chlorine products revert rapidly at room temperature and must be separated during photolysis in order to achieve a practical photostationary state.

Splitter and Calvin were the first to suggest[13] that electronic excitation energy could be stored as chemical potential energy through the photochemical formation of small strained rings. Their example involved the photochemical ring closure of N-alkyl-X-arylnitrones (7 → 8) which is thermally reversible. The photochemical step is generally observed[14] and is suitably photochromic (nitrone absorption in the 300 - 500 nm range).[14,15] The quantum efficiency for ring closure is respectable (ϕ = 0.2 - 0.5),[15] and the thermal back reaction of the oxaziridine photoproducts (e.g., 8) occurs at useful temperatures in some cases.[16] The amount of energy stored is unknown, but reflected in the enthalpy for ring closure will be a large strain energy, quite generally assumed for small rings to be about 25 kcal/mol.[8]



7 8



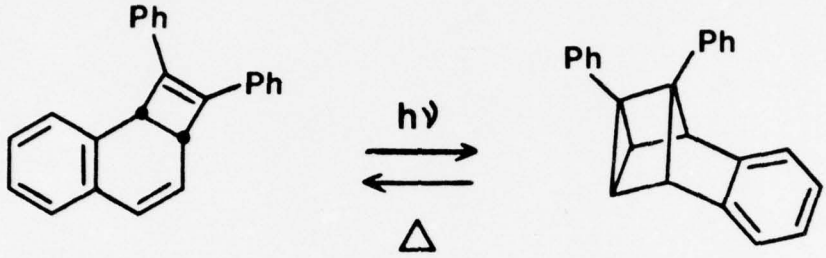
9 10

The report of Cristol and Snell[17] concerning the isomerization 9 ⇄ 10 (R = CO_2H) is an early example of photon energy storage which may be reversed under catalysis conditions. The parent norbornadiene, 9 (R = H), has received considerable attention following the pioneering quantitative study of Hammond and coworkers.[18] High quantum efficiencies for direct photoisomerization of norbornadiene derivatives[19] ($\phi \sim 0.5$) and for isomerization using a variety of photosensitizers (ϕ = 0.1 - 1.0)[20] have been reported. The energy rich isomer, quadricyclene (10, R = H) is thermally stable to 150°,[21] but can be reverted using a variety of metal catalysts over a range of temperatures.[22] The heat liberated in the back reaction of 10 is impressive (R = H, ΔH = -26.2 kcal/mol, 285 cal/g, 25°).[23] Recent important advances for the norbornadiene system include the use of polymer supported sensitizers for driving the photoisomerization in the 300 - 400 nm range with quantum yields of 0.5[24] and the development of inorganic complexing agents (e.g., Cu(I)) for the enhancement of spectral sensitivity.[25]

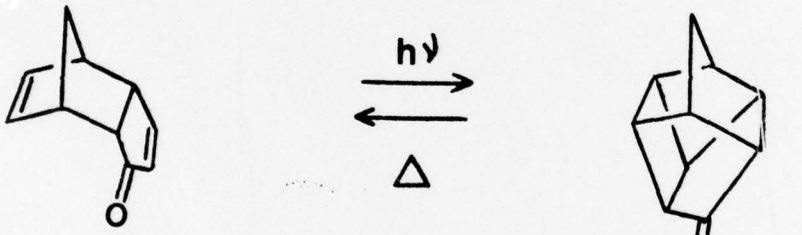
A measure of energy storage capacity and efficiency for these energy storing photoreactions is the calculated "Q value" as suggested by Calvert.[3b]

$$Q = \frac{100\ \Delta H\ \phi}{E_\lambda}$$

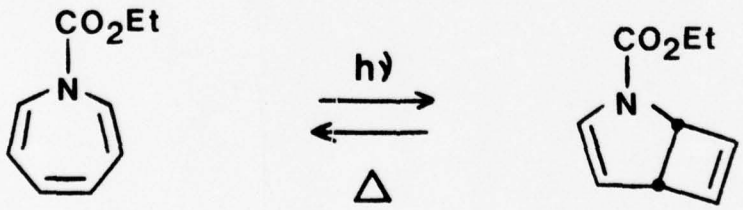
where Q represents a percent efficiency, ΔH is the standard enthalpy increase for the overall chemical reaction (A → B) (Calvert uses latent free energy[3b]), ϕ is the quantum efficiency for formation of product B, and E is photon energy (kcal/Einstein) for an appropriate wavelength of absorbed radiation. The latter is often associated with an absorption maximum or band edge or with a lamp emission wavelength, although the relevant quantity in terms of solar energy use is an integration of solar photon energy and distribution. Data for a number of endoergic photoreactions are collected in Table II, including energy



11 12



13 14



15 16

Table II. Some Energy Storing Photoreactions and Their Efficiencies

Reaction	Effective Wavelength (nm)[a]	Quantum Yield	ΔH, kcal/mol (cal/g)	Q Value % Efficiency
$NOCl \rightarrow NO + 1/2\ Cl_2$	600	1.0	4.9 (75)	11
9 → 10 (R + H)	366[c]	0.5	26.2 (285)	17
9 → 10 ($R = CO_2Me$)	334	0.5	18.5 (89)[d]	11
11 → 12	366	0.3	29.0 (95)	11
13 → 14	366	0.4	16.4 (112)	8
15 → 16	458	0.013	10.4 (63)	0.2

[a] Generally, the longest wavelengths reported to be useful. [b] Reaction enthalpies from combustion or differential scanning calorimetry data (temperatures ranging from 25 to 200°). [c] Photosensitizer used, ref 23. [d] Ref 29.

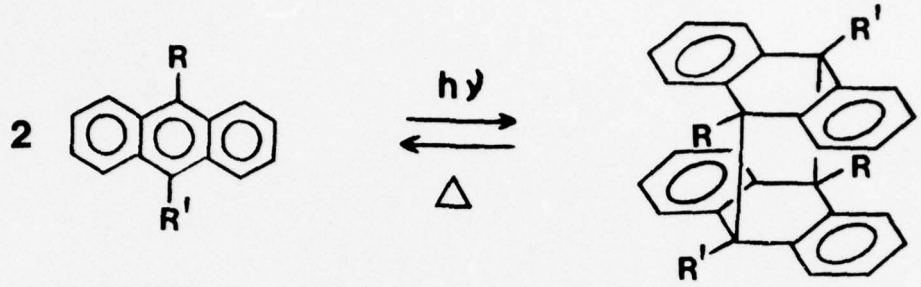
storage parameters for the isomerization of 11 studied by Sasse[26] and the isomerizations of 13[27] and 15,[28] which have been evaluated by Jones and coworkers.

VALENCE PHOTOISOMERIZATION OF LINKED ANTHRACENES

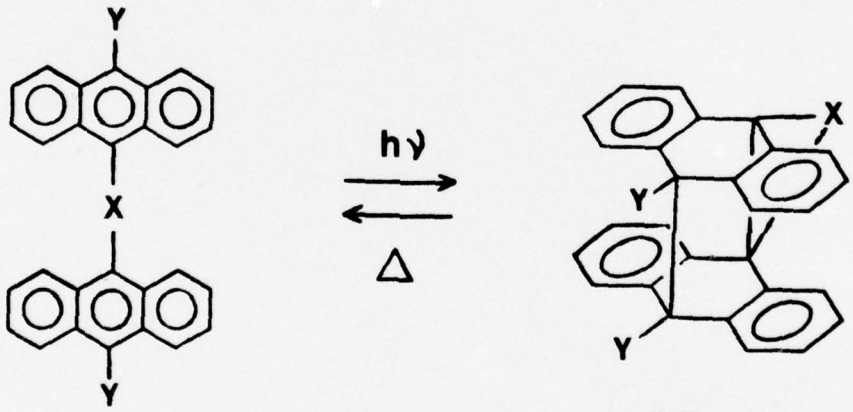
The photodimerization of anthracene (17 → 18, R = H) is the organic system first cited as an example of the conversion of light energy into chemical potential energy.[30] Anthracene and its derivatives, which absorb strongly around 400 nm, are photobleached in sunlight. Photodimers of varied structure[31] are produced in high chemical yield and absorb light only below 300 nm. The quantum efficiency for photodimerization is concentration dependent, approaching 0.3 at high anthracene concentrations.[32] Photodimers revert thermally to monomer anthracenes either in the solid state or in solution with rates which depend on the substitution pattern at bridge positions.[31a] The conditions and heats for back reactions for several examples are shown in Table III.

The intramolecular photoaddition of anthracene groups has been reported.[31a,33] We have studied a number of these isomerizations (19 → 20 and 21 → 22), encouraged that advantages were to be gained over the intermolecular examples. (1) Quantum efficiencies for isomerization of linked anthracenes should be independent of concentration. (2) Improved light absorption might result from interchromophore interaction in special cases. (3) Higher storage enthalpies might be found where internal photoaddition requires formation of a strained three or four-membered ring as the result of anthracene linkage.

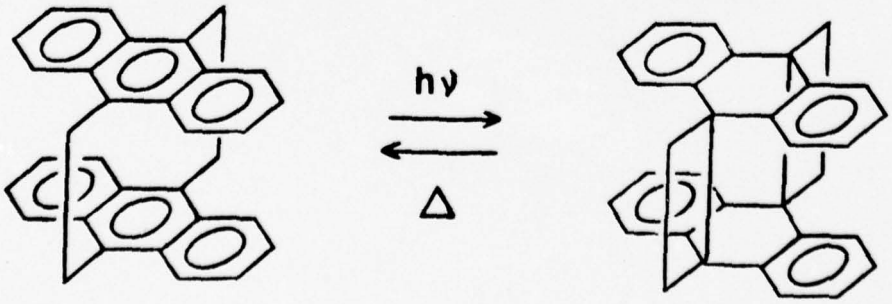
Isomerizations 19 → 20 are quantitative on irradiation at 366 nm in dilute benzene solution. Quantum yields for linked anthracene photoisomerization (ϕ, forward) and fluorescence (a process which competes for depletion of excited states) are shown in Table IV. Interestingly, photoisomers 20 and 22 revert photochemically (quantum efficiencies, ϕ_{back}, Table IV) as well as thermally, but irradiation at short wavelengths is required for photochemical back reaction



17 18



19 20



21 22

Table III. Thermal Back Reaction of Anthracene Photodimers

	Temperature Range (°C)	ΔH, kcal/mol[a] (cal/g)	Arrhenius Parameters[b] E_a (kcal/mol)	Log A
17 ← 18 (R = R' - H)		15.6 (45)[c]		
17 ← 18 (R = H, R' = CN)	125 - 150	20.0 (49)[d]		
17 ← 18 (R = OAc, R' = CN)	35 - 65	19.7 (37)[d]		
19 ← 20 (X = CH_2, Y = H)	130 - 150	17.3 (50)	32.7	15.4
19 ← 20 (X = CH_2CH_2, Y = H)	120 - 135	14.6 (38)	32.8	15.9
21 ← 22	50 - 70	8.5 (21)	22.3	12.2

[a]Measured by differential scanning calorimetry except where noted. [b]Calculated from the temperature dependence of the rate constant for back reaction using the Arrhenius equation, $\log k = \log A - E_a/2.3\ RT$. [c]Calculated from experimental heats of combustion for 17 and 18 (R = R' = H), ref 35. [d]Ref 36.

Table IV. Photochemical, Photophysical, and Energy Storage Data for Linked Anthracenes.

			$\phi^{a}_{forward}$	ϕ^{b}_{back}	ϕ^{c}_{f}	Q Value[d] % Efficiency
	19 ⇌ 20					
	X	Y				
(a)	CH_2CH_2	H,H	0.26	0.55	0.16	5.2
(b)	CH_2CH_2	CH_3,CH_3	0.04	--	0.14	--
(c)	CH_2	H,H	0.15	0.76	0.06	3.6
(d)	CHOH	H,H	0.29	0.81	0.02	--
(e)	CHOH	H,OCH_3	0.05	--	0.02	--
	21 ⇌ 22		0.36	0.60[e]	< 0.001	5.4[f]

[a]Quantum yield for forward isomerization (e.g., 19 → 20), 366 nm. [b]Quantum yield for back isomerization (e.g., 30 → 19), 285 nm. [c]Quantum yield of fluorescence (benzene solution, excitation 366 nm). [d]Photon energy storage efficiency for forward isomerization, calculated using enthalpy values from Table III, $\phi_{forward}$, and E_λ = 73 kcal/Einstein (390 nm), except where noted. [e]Ref 33 f,g. [f]Calculated using E_λ = 57 kcal/Einstein (500 nm).

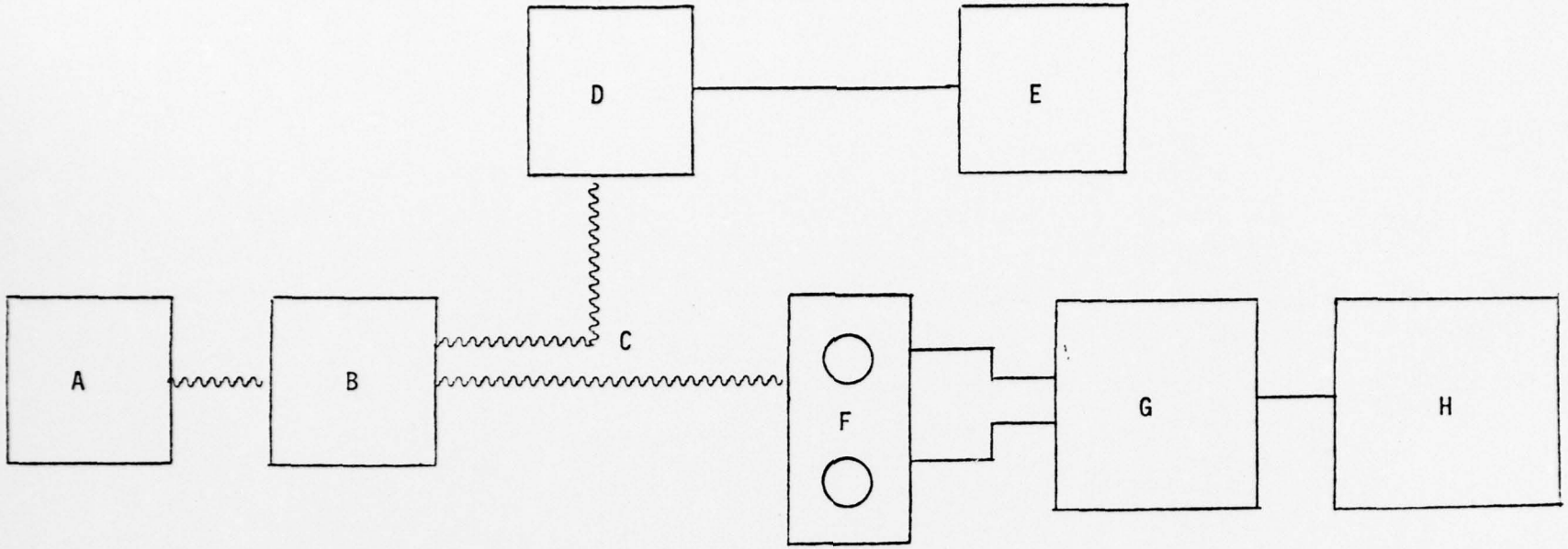
since the cage photoisomers absorb only below 300 nm. Quantum efficiencies for forward and reverse photoisomerization and linked anthracene fluorescence sum to unity (within experimental error). This behavior is consistent with a mechanism, which we have proposed elsewhere,[34] involving an intermediate which is common to photoisomerization in both directions and whose partitioning controls the efficiencies of forward and back reaction.

Linked anthracenes 19 do not show unusual absorption due to chromophore interaction (principal λ_{max} 390 nm). However, the doubly bridged paracyclophane derivative 21 is orange in color and absorbs significantly past 500 nm.[37] This interesting compound is rapidly bleached in sunlight and photoisomerization can be readily carried out using 458 nm radiation from an argon-ion laser.

Data are included in Table III for the thermal back reaction of photoisomers 20 and 22. Recycling of the energy rich isomers is clean and virtually quantitative in solvents such as o-dichlorobenzene. Sequential photochemical and thermal reactions have been carried out on a small scale using artificial light sources or sunlight for the irradiation step. Without resorting to special methods of purification of materials, as many as ten photo-thermal cycles may be completed, although UV spectral monitoring of regenerated linked anthracene absorbance shows some material degradation.

PHOTOCALORIMETRY

Differential scanning calorimetry (DSC) has been used to measure the heat of thermal back reaction for selected isomers 20 and 22 (see Table IV for calculated Q values). For reversion <u>in the solid state</u>, values obtained (Table III) appear unpredictably low, in view of the reported enthalpy for reversion of dianthracene (18 → 17, R = H) and anticipating additional release of ring strain in 20 and 22 (vide supra). The insolubility of linked anthracenes precludes DSC experiments in solution.



A Super pressure Hg lamp

B B and L High Intensity Monochromator

C Quartz optical fiber light conductors

D Quantum counter

E Digital integrator

F Two cell calorimeter

G Amplifier

H Recorder

An apparatus has been constructed (Scheme 1) which allows direct measurement of stored photon energy in a solution experiment. The calorimeter is similar to one previously described,[38] but modified for the introduction of light from a monochromatic source. Heat effects (measured with thermistor probes and calibrated against electrical resistance heating) for irradiation of a solution sample capable of undergoing photochemical reaction (e.g., 19 → 20) are compared with those for irradiation of an unreactive sample converts photon energy into heat (normally benzophenone in benzene, excitation at 366 nm). Precautions are taken to insure that light incident on the samples is completely absorbed. Photocalorimetrically determined values for the enthalpy of reaction 20 → 19 (X = CH_2, Y = H) are consistently upwards of 25 kcal/mol, consonant with the expectation that data for reversion in the solid state reflect values which are biased due to differential heats of sublimation[31a] for the valence isomers. Unfortunately, data collected so far show considerable scatter (± 25%) and a reliable determination of the heats of reaction in solution for the linked anthracene systems awaits improvement in calorimeter sensitivity (presently, 0.01 cal/min).

Procedures for the measurement of photochemical or photophysical heat effects have been known for some time. Early values for the quantum yield of photosynthesis in algae were obtained by photocalorimetry.[39] A novel method for the determination of fluorescence quantum yields employing heat effects has been reported by Seybold.[40] In a somwhat different application, enthalpies for reaction of unstable photochemical products have been measured by differential thermal analysis.[41] The development of the photocalorimetry technique for the ready determination of latent heat storage capacities of photoproducts is surely warranted.

PROSPECTUS

The economic and engineering requirements for a hypothetical photochemical solar-thermal transducer have been examined.[5,42] Advantages noted include lower

collector size and cost, lower collector temperature (reduced heat loss and insulation requirements), smaller storage area, and improved adverse weather performance (cloudy day effectiveness, storage at ambient temperature).

Most notable about selected organic valence isomerizations are their relatively large storage enthalpies, their unidirectional photochemistry at long wavelengths (desirable photochromism due to the destruction of pi systems), and the kinetic stability of energy-rich photoproducts. Additionally, some isomerizations (e.g., 9 → 10 and 13 → 14) may be reversed using homogeneous or heterogeneous catalysts, offering opportunities for chemical engineering of a cyclic system capable of delivering heat at different temperatures. A simple plan, following earlier suggestions,[6,24] for a photochemical solar-thermal energy conversion unit is shown in Scheme II. The design incorporates polymer supported[24] photosensitizer and reversion catalyst materials for heterogeneous activation of a working fluid. The system could in principle store sensible as well as latent heat.[42]

Characteristics of energy storing organic photoreactions are well illustrated in the examples cited above. None of the systems, however, approach fulfillment of criteria for the efficient storage and conversion of solar energy. All of the photoreactions studied so far are principally deficient in utilizing the solar insolation spectrum. Also, extensive recycle capability has not been demonstrated, although organic isomerizations are known[43] which impressively survive repeated reaction on a small scale in solution.

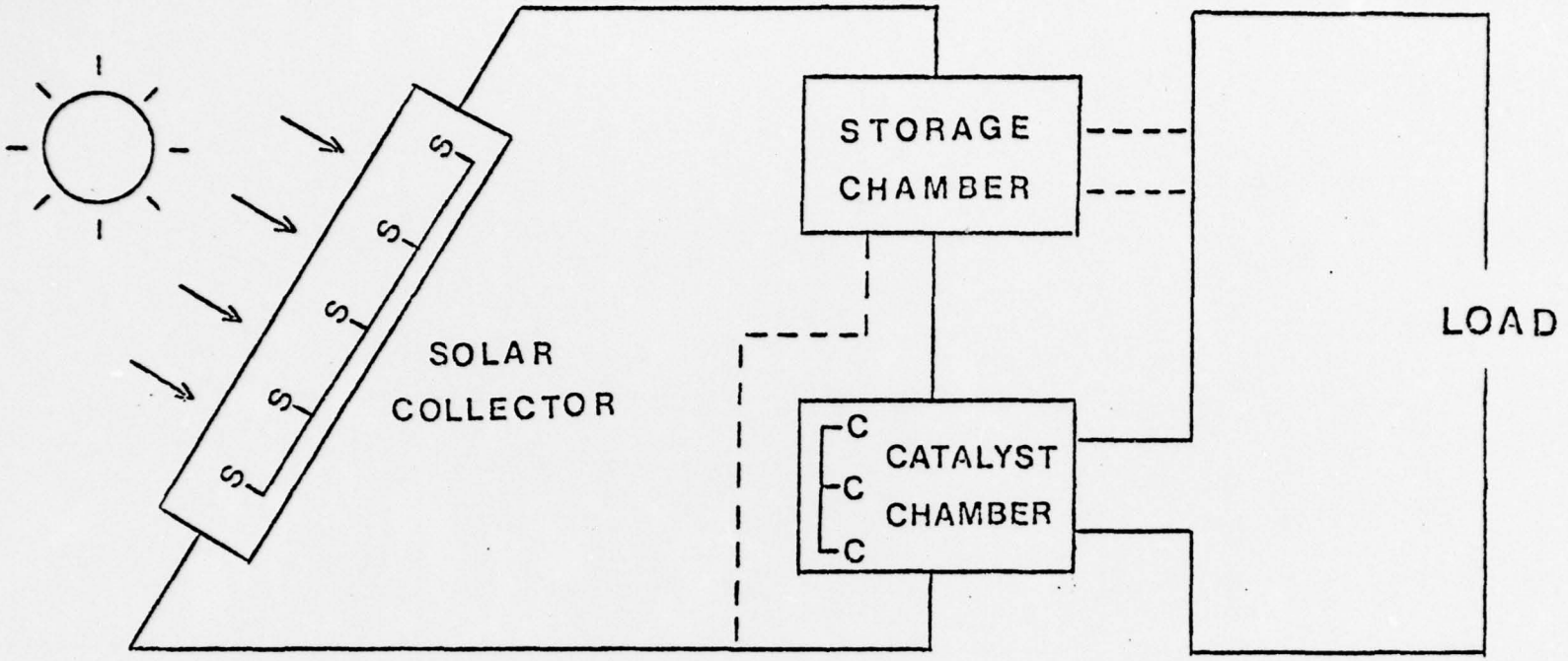
Comparison of the energy storage capacities of several relevant materials is shown in Table V. The energy density of hot water or rocks is not high, but the costs of these sensible heat storage materials is low, relative to collector and other costs for a conventional solar-thermal system, and cycles of heating and cooling may be repeated indefinitely. The economics for latent heat storage materials will be determined not only by raw material costs but

Table V. Energy Storage Capacities of Materials

MATERIAL	KCAL/MOL	CAL/G	BTU/LB
SENSIBLE HEAT STORAGE			
WATER (ΔT = 50°C)	0.9	50	91
ROCK, METAL (ΔT = 50°C)		10	18
LATENT HEAT STORAGE			
$C_6H_{12}O_6$ CARBOHYDRATE (COMBUSTION)	673	3,740	6,800
C_{10} HYDROCARBON (COMBUSTION)	1,500	11,000	20,000
GLAUBER'S SALT (1 CYCLE)	11	60	108
(100 CYCLES)		6,000	10,800
ORGANIC VALENCE ISOMER (1 CYCLE)	20	133	240
(MW 150) (100 CYCLES)		13,300	24,000

also by the number of energy storage cycles that may be achieved. The model here is a phase change material such as sodium sulfate decahydrate (Glauber's salt), one of a number of inorganic chemicals whose energy-storing fusion properties are currently under examination by solar engineers.[44] These materials have relatively high energy density, are inexpensive ($\sim$ \$0.10/lb), and have other properties suitable for use in forced air heating systems. On the other hand, heats of fusion for the salts diminish on repeated cycling due to incongruent melting, and the deliver of heat is at a fixed and generally low temperature (30 - 40°).[44a]

The unit of merit for the storage of solar energy as sensible or latent heat is 10^6 Btu (2.5×10^5 kcal).[44b] This figure approximates the energy of atmospherically filtered solar radiation incident daily on a conventional



S = PHOTOSENSITIZER

C = CATALYST

(rooftop) flat-plate collector ($\sim$ 100 m^2) in North American latitudes.[45] One million Btu also corresponds roughly to the daily heating load in winter for an average dwelling in a moderately cold climate.[46] The amount of a chemical required for the storage of 10^6 Btu as latent heat is 4200 lb (2000 kg or about 500 gal of a neat liquid), assuming a capacity of 20 kcal (80 Btu)/mol and 3 mol/lb. This simple calculation readily shows that material requirements for practical chemical storage of solar energy are quite large.

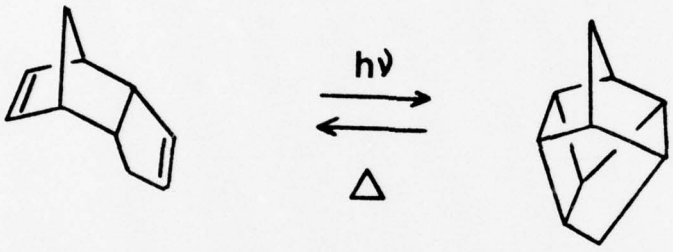
An organic valence isomerization system (with storage enthalpy = 20 kcal/mol) is competitive with other storage materials on energy density grounds alone. Included in Table V for comparison are storage capacities of photosynthetic fuels (a carbohydrate and a hydrocarbon of molecular weight comparable to the proposed valence isomer system) which have sizeable latent heats of combustion. The added perspective is that many cycles of photo-thermal conversion of an organic isomerization system are required to produce the energy equivalent to that generated by simply burning the same material.

The cost restrictions for a latent heat storage chemical are also severe. Economic studies suggest a "cost allowance" for storage raw material of \$2,000/10^6 Btu.[44b] This figure is amortized over three years, or about 300 (10^6 Btu) heating cycles. An organic material ($\sim$ 5000 lb) costing \$0.10 - 0.40/lb would meet this requirement. For comparison, salt hydrates which have been surveyed[44b] have storage costs of \$100 - 770 and storage weights of 8,800 - 13,300 lb for repeated delivery of 10^6 Btu.

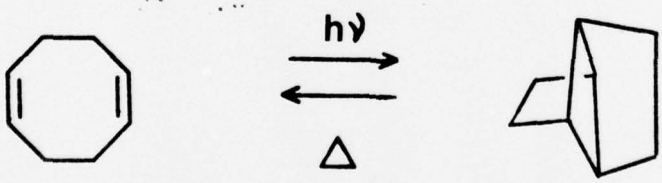
The analysis of the organic isomerization does not include, of course, the cost of other materials (photosensitizers, catalysts) which may be necessary for a photochemical-thermal system. A reasonable plan (Scheme II) would require these additives in a volume which is lower and for a lifetime which is perhaps longer than the storage chemical itself. Nonetheless, costs of the activating agents will be non-trivial, although presently difficult to project.

The number of large-scale industrial chemicals available at an appropriate cost and scale, which have some potential for photochemical energy storage, is quite small. Norbornadiene (9, R = H), although not presently manufactured, warrants further attention due to its ready availability from cyclopentadiene and acetylene. Dicyclopentadiene, which is known to undergo photosensitized valence isomerization (23 → 24),[57] is available on a large scale (@ $0.12/lb) from the cracking of gas oil and naphtha. Its use would not detract from a diminishing supply of key petrochemical intermediates since it is expected to be in oversupply in coming years.[48] Another interesting candidate is 1,5-cyclooctadiene (25) which is prepared industrially by dimerization of butadiene. Metal complexing agents (Cu) have been shown to improve the spectral sensitivity of 25 and to promote isomerization to valence isomer 26.[49] Cyclooctadiene could assume importance as a storage material for long range use due to the practicality[50] of the sequence, ethanol → butadiene → cyclooctadiene which is not petroleum based. Studies of the sensitized photoisomerization of these commercially important hydrocarbon dienes are currently underway in our laboratories.

Acknowledgements - This work was supported by the Office of Naval Research and the National Science Foundation (through a fellowship to W.R.B.). We thank J. Kung, B.R. Ramachandran, L.J. Turbini, R.E. Richmond, and A.H. Pachtman for technical assistance.



23 24



25 26

REFERENCES

(1) Presented in part at the 1st International Conference on the Photochemical Conversion and Storage of Solar Energy, London, Ontario, Canada, August 24 - 28, 1976, abstract G4.

(2) (a) Boston University; (b) Ithaca College.

(3) (a) F. Daniels, "Direct Use of the Sun's Energy," Yale University Press, New Haven, 1964, chp 17; (b) J.G. Calvert in "Introduction to the Utilization of Solar Energy," A.M. Zarem, Ed., McGraw-Hill Book Co., N.Y., 1963, chp9; (c) R.J. Marcus, Science, 123, 399 (1956); (d) G. Stein, Israel J. Chem., 14, 213 (1975); (e) V. Balzani, L. Moggi, M.F. Manfrin, F. Bolletta, and M. Gleria, Science, 189, 852 (1975).

(4) (a) D.E. Hall, J.A. Eckert, N.N. Lichtin, and P.D. Wildes, J. Electrochem. Soc., 123, 1705 (1976); (b) M.D. Archer, J. Appl. Electrochem., 5, 17 (1975); (c) P.D. Wildes, N.N. Lichtin, M.Z. Hoffman, L. Andrews, and H. Linschitz, Photochem. and Photobiol., in press.

(5) R.E. Schwerzel and J.R. Hoyland, International Conference on the Photochemical Conversion and Storage of Solar Energy, London, Ontario, Canada, August 24 - 28, 1976, abstract G3.

(6) G. Jones, II, NSF/RANN Workshop Report, "The Current State of Knowledge of Photochemical Formation of Fuel," N.N. Lichtin, Ed., Boston University, 1974.

(7) W.E. Wentworth and E. Chen, Solar Energy, 18, 205 (1976).

(8) J.F. Liebman and A. Greenburg, Chem. Rev., 76, 311 (1976).

(9) S.W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, 1968, chp 2.

(10) Consult articles in "Orbital Symmetry Papers," H.E. Simmons and J.F. Bunnett, Ed., American Chemical Society, Washington, 1974.

(11) For a collection of examples, see R.B. Woodward and R. Hoffmann, Angew Chem. Intern. Ed. Engl., 8, 847 (1969).

(12) R.J. Marcus and H.C. Wohlers, Solar Energy, 5, 44 (1961)

(13) J.S. Splitter and M. Calvin, J. Org. Chem., 23, 65 (1958).

(14) (a) J.S. Splitter and M. Calvin, ibid., 33, 3427 (1965); (b) G.G. Spence, E.C. Taylor, and O. Buchardt, Chem. Rev., 70, 231 (1970).

(15) K. Koyano, H. Suzuki, Y. Mori, and I. Tanaka, Bull. Chem. Soc. Japan, 43, 3582 (1970).

(16) M.F. Hawthorne and R.D. Strahm, J. Org. Chem., 22, 1263 (1957).

(17) S.J. Cristol and R.L. Snell, J. Am. Chem. Soc., 76, 5000 (1954).

(18) G.S. Hammond, P. Wyatt, C.D. DeBoer, and N.J. Turro, J. Am. Chem. Soc., 86, 2532 (1964).

(19) (a) G. Kaupp and H. Prinzbach, Chem. Ber., 104, 182 (1971); (b) Helv. Chim Acta 52, 956 (1969).

(20) For leading references see A.A. Gorman, R.L. Leyland, M.A.J. Rodgers, and P.G. Smith, Tetrahedron Lett., 5085 (1973).

(21) H.M. Frey, J. Chem. Soc., 365 (1964).

(22) K.C. Bishop, III, Chem. Rev., 76, 461 (1976).

(23) K.B. Wiberg and H.A. Connon, J. Am. Chem. Soc., 98, 5411 (1976).

(24) R.R. Hautala, J. Little, and E. Sweet, Solar Energy, in press.

(25) C. Kutal and D.P. Schwendiman, Solar Energy, in press.

(26) (a) P.J. Collin and W.H.F. Sasse, Aust. J. Chem., 24, 2325 (1971); (b) W.H.F. Sasse, Solar Energy, in press.

(27) (a) G. Jones, II and B.R. Ramachandran, J. Org. Chem., 41, 796 (1976); (b) G. Jones, II and B.R. Ramachandran, J. Photochem., 5, 341 (1976).

(28) G. Jones, II and L.J. Turbini, J. Org. Chem., 41, 2362 (1976).

(29) D.S. Kabakoff, J.-C.G. Bunzli, J.R.M. Oth, W.B. Hammond, and J.A. Berson, J. Am. Chem. Soc., 97, 1510 (1975).

(30) F. Weigert, Eder's Jahrb., 111 (1909); Chem. Abstr., 4, 3170 (1910).

(31) (a) F.D. Greene, Bull. Soc. Chim. France, 1356 (1960); (b) R. LaLande and R. Calas, ibid., 144, 148 (1960); (c) A. Castellan, R. Lapouyade, and H. Bouas-Laurent, ibid., 8 (1976).

(32) N.C. Yang, D.M. Shold, B. Kim, J. Am. Chem. Soc., 98, 6587 (1976).

(33) R. Livingston and K.S. Wei, J. Am. Chem. Soc., 89, 3098 (1967); (b) N.M. Weinshenker and F.D. Greene, ibid., 90, 506 (1968); (c) S.J. Cristol and J.S. Perry, Tetrahedron Lett., 1921 (1974); (d) D.E. Applequist and D.J. Swart, J. Org. Chem., 40, 1800 (1975); (e) G. Felix, R. Lapouyade, H. Bouas-Laurent and B. Clin, Tetrahedron Lett., 2277 (1976); (f) G. Kaupp, Ann., 844 (1973); and (g) G. Kaupp, Angew Chem. Intl. Ed. Engl., 11, 313 (1972).

(34) G. Jones, II, 12th Informal Conference on Photochemistry, National Bureau of Standards, Gaithersburg, Md., June 28 - July 1, 1976, abstract I2; W.R. Bergmark and G. Jones, II, submitted.

(35) P. Bender and J. Farber, J. Am. Chem. Soc., 74, 1450 (1952).

(36) (a) G. Guarini and P. Sarti-Fantoni, Mol. Crystals and Liquid Crystals, 6, 423 (1970); (b) D. Donati, G. Guarini, and P. Sarti-Fantoni, ibid., 17, 187 (1972).

(37) J.H. Golden, J. Chem. Soc., 3741 (1961).

(38) E.M. Arnett, W.G. Bentrude, J.J. Burke, and P.M. Duggleby, J. Am. Chem. Soc., 87, 1541 (1965).

(39) J.L. Magee, T.W. DeWitt, E.C. Smith, and R. Daniels, J. Am. Chem. Soc., 61, 3529 (1939).

(40) P.G. Seybold, M. Gouterman, and J. Callis, Photochem., and Photobiol., 9, 229 (1969).

(41) E. Koch, Angew. Chem. Intl. Ed. Engl., 9, 288 (1970).

(42) S.G. Talbert, D.H. Friesling, J.A. Eibling, and R.A. Nathan, Solar Energy, 17, 367 (1975).

(43) G.A. Doorakian and H.H. Freedman, J. Am. Chem. Soc., 90, 5310, 6896 (1968).

(44) (a) H.G. Lorsch, K.W. Kauffman, and J.C. Denton, Energy Conversion, 15, 1 (1975); (b) M. Telkes, ASHRAE Journal, 38 (1974).

(45) Ref 3a, chp 2.

(46) J.A. Duffie and W.A. Beckman, "Solar Energy Thermal Processes," John Wiley and Sons, New York, 1974, chp 12.

(47) (a) W.L. Dilling, J. Org. Chem., 40, 2380 (1975); (b) G.O. Schenck and R. Steinmetz, Chem. Ber., 96, 520 (1963).

(48) "Hydrocarbon Processing," September, 1976, p 235.

(49) (a) G.M. Whitesides, G.L. Goe, and A.C. Cope, J. Am. Chem. Soc., 91, 2608 (1969); (b) R.G. Salomon and J.K. Kochi, Tetrahedron Lett., 2529 (1973).

(50) I.S. Goldstein, Science, 189, 847 (1975).

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 102IP	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, Rm. 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
ONR Branch Office 495 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1
Director, Naval Research Laboratory Washington, D. C. 20390 Attn: Library, Code 2029 (ONRL) Technical Info. Div. Code 6100, 6170	6 1 1
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D. C. 20360 Attn: Code 310C (H. Rosenwasser)	1

	No. Copies
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U. S. Army Research Office P. O. Box 12211 Research Triangle Park, North Carolina 27709	1
Commander Naval Undersea Research & Development Center San Diego, California 92132 Attn: Technical Library, Code 133	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W. S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D. C. 20380	1
Advanced Research Projects Agency Materials Sciences Office 1400 Wilson Boulevard Arlington, Virginia 22209 Attn: Dr. Stan Ruby	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. M. A. El-Sayed University of California Department of Chemistry Los Angeles, California 90024	1
Dr. M. W. Windsor Washington State University Department of Chemistry Pullman, Washington 99163	
Dr. E. R. Bernstein Colorado State University Department of Chemistry Fort Collins, Colorado 80521	
Dr. C. A. Heller Naval Weapons Center Code 6059 China Lake, California 93555	1
Dr. M. H. Chisholm Chemistry Department Princeton, New Jersey 08540	1
Dr. J. R. MacDonald Code 6110 Chemistry Division Naval Research Laboratory Washington, D. C. 20375	1
Dr. G. B. Schuster Chemistry Department University of Illinois Urbana, Illinois 61801	1
Dr. E. M. Eyring University of Utah Department of Chemistry Salt Lake City, Utah	1
Dr. A. Adamson University of Southern California Department of Chemistry Los Angeles, California 90007	1
Dr. M. S. Wrighton Massachusetts Institute of Technology Department of Chemistry Cambridge, Massachusetts 02139	1